



Selective Fluorescence Chemosensor for Al³⁺ based on Antipyrine with Furfural Attached Allyl System

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ABSTRACT

By incorporating Furfural-Antipyrine as coordinate sites into the fragment of receptor FBH-AP has been used as an artificial chemosensor for selective recognition of transition metals. The strong fluorescence emission at 388 nm of the receptor FBH-AP is effectively and selectively quenched by Al³⁺. A 1:1 complex is formed between the FBH-AP and Al³⁺ is determined by jobs plot and their common interferent ions do not show any interference with the Al³⁺. It is anticipated that the antipyrine could be a good candidate probe and has potential application for Al³⁺ determination.

Keywords: Fluorescence Chemosensor; Al³⁺; Antipyrine.

1. INTRODUCTION

The design and synthesis of organic material used as a fluorescent chemosensor for selective recognition of transition metal ions have received special attention in the last decades due to the essential roles that cations play in biology, environmental chemistry, and food safety (Rurack *et al.* 2002; Kim *et al.* 2011a; Vengaiyan *et al.* 2015; Yin *et al.* 2015). Current researches prefer the fluorescence chemosensor for its exclusive qualities are sensitivity, selectivity, direct visual observation, and immediate replica (Kim *et al.* 2011b) and utilized in a variety of applications such as molecular devices (Pischel *et al.* 2007), nerve gas sensor (Burnworth *et al.* 2007), biological probes, environmental sensors (Kim *et al.* 2007) and pH sensor (Han *et al.* 2010). A suitable scaffold is required to anchor the binding sites close to interacting with cations (Kim *et al.* 2015).

The recognition of antipyrine derivatives is essential for pharmacological and clinical applications, including antifungal, antibacterial, antipyretic, analgesic, anti-inflammatory as well as antitumor activity. It was chosen the fluorophore, the signalling unit particularly carbonyl oxygen and nitrogen of the amine act as binding sites provides excellent photophysical properties such as good photostability, strong absorption, and emission signals (Dessingou *et al.* 2012; Gupta *et al.* 2014b; Selvan *et al.* 2018; Tamil Selvan *et al.* 2020). Baylis Hillman reaction is one of the most profit-making C-C bond formations and its functionalities are used as an intermediate for multiple organic transformations. In the series, C-N formation by using various nucleophiles with

Baylis Hillman adduct or acetate is special attention (Shanmugam *et al.* 2002; Shanmugam *et al.* 2004; Shanmugam *et al.* 2005). Heterocycle scaffold is most attractive and strong binding affinity with cations are widely employed in the construction of chemosensors (Guo *et al.* 2007; Maity *et al.* 2012; Chebrolu *et al.* 2014; Cheng *et al.* 2016).

Being the third most abundant metal, aluminium is widespread in the environment, particularly on the earth's crust. Due to its widespread use as food additives, in aluminium-based pharmaceuticals, and storage utensils, human beings are constantly being exposed to toxic levels of aluminium. Though Al³⁺ has so many positives the negatives should also be taken into consideration. World health organization recommended the aluminium concentration in our daily intake is 3-10 mg, the excess of aluminium leads to damage to the central nervous system, parkinson's disease, and Alzheimer's disease (Andrási *et al.* 2005; Kaur *et al.* 2012; Gupta *et al.* 2014a). In agriculture, the release of aluminium ions from acidic soils is toxic to plant roots (Ahmad *et al.* 2002). Therefore It is important that aluminium concentrations in the permissible level, in light of this need for constant monitoring of human in vivo and environmental aluminium concentrations, we report the efforts undertaken in designing Al³⁺ sensors (Kim *et al.* 2012; Datta *et al.* 2013; Helal *et al.* 2013). Several Al (III) sensors have been reported in the literature (Saini *et al.* 2016; Selvan *et al.* 2018).

Recently our group reported (E)-cinnamic ester with antipyrine fluorescence chemosensor act as ONO tridentate for the detection of Zn²⁺ ions (Banumathi *et al.*

2020). The benzene aromatic scaffold of our previously reported BH-AP compound is replaced by a heterocycles scaffold to know the coordination ability of metal ions. The above-mentioned importance of antipyrine and heterocycles keep in our mind, we were interested in designing the probe having a heterocycle coordinate site for cation binding by connecting two of them. Herein we have designed and synthesised Baylis Hillman derivatives having furfural ring and antipyrine FBH-AP, which showed potential to be a highly selective fluorescent chemosensor for Al^{3+} ions.

2. EXPERIMENTAL SECTION

2.1 Chemical and instruments

All reagents, chemicals, and solvents were of analytical grade and double-distilled water was used throughout the analysis; Furfuraldehyde, ethyl acrylate, DABCO, acetyl chloride, pyridine, and 4-aminoantipyrine were purchased from Sigma-Aldrich, India, solvents including ethyl acetate, ethanol, DMSO, DMF, acetonitrile, and chloroform, were obtained from Finar, India. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz FT-NMR spectrometer respectively, in CDCl_3 solution with TMS as internal standard. IR spectra were recorded on a Bruker FT-IR spectrometer. Fluorescence measurements were performed on a dual-beam UV-Visible spectrophotometer (JASCOV-630), the fluorescence analysis was performed on a fluorescence spectrometer (JASCO FP-8300) equipped with quartz cuvettes of 1 cm path length. The excitation and emission slit widths were 5.0 nm.

2.2 Synthesis of receptor FBH-AP

The starting compound BH-Ac was prepared using the literature procedure. Then designed FBH-AP from, FBH-Ac (100 mg, 0.4 mmol) and 4 amino antipyrine (1eq, 0.0789 g), were taken in 2 ml of ethanol and the reaction mixture was heated at 60°C for 12 hours. After the completion of the reaction, the product was separated by using water and ethyl acetate and dried over anhydrous Na_2SO_4 . After evaporation of the solvent under vacuum, the product FBH-AP was obtained as dark

brown colour oil in 80% yield. It was further purified using silica gel column chromatography taking ethyl acetate and hexane mixture (1:4) as eluent.

2.3 Studies on metal ions sensing

To check the cations binding property of the receptor, stock solutions for analysis and various metal ion solutions were prepared ($1 \times 10^{-3}\text{ M}$) from the sulphate and nitrate salts of K^+ , Al^{3+} , Cu^{2+} , Cd^{2+} , Co^{2+} , Ca^{2+} , Mn^{2+} , Cr^{3+} , Mg^{2+} , Fe^{2+} , and Fe^{3+} immediately before the experiments. The UV- Vis and fluorescence

spectrum was recorded by adding 100 μl of FBH-AP with 100 μl of metal solutions from their stock solutions was mixed in $\text{DMF}/\text{H}_2\text{O}$ (1:9 (v/v) at $\text{pH} = 7.0$ (Selvan *et al.* 2018). The cationic recognition property was calculated from variations in the fluorescence spectrum of receptor FBH-AP in the existence of other metal ions.

2.4 Studies on competitive binding

Fluorescence spectrum was recorded by adding 100 μl of FBH-AP with 100 μl of other metal solutions and 100 μl of sensing metal Al^{3+} ions were mixed and made up to 10 ml of water (Tamil Selvan *et al.* 2018).

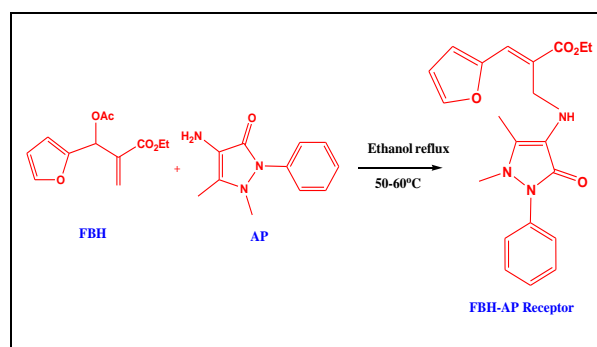
2.5 Jobs plot

The binding stoichiometry of FBH-AP with Al^{3+} ions was studied by using a dilute concentration of a metal solution from 0.1 to 1.0 with a constant concentration of 100 μl of FBH-AP were mixed and made up to 5 ml of water. The mole fraction of Al^{3+} calculated as, Mole fraction= $[\text{Al}^{3+}] / [\text{FBH-AP} + \text{Al}^{3+}]$.

3. RESULT AND DISCUSSION

3.1 Synthesis and characterization of Receptor FBH-AP

The receptor FBH-AP was concisely synthesized from acetate of 2-Furfuraldehyde Baylis Hillman adduct with 4 amino antipyrine (1eq) through a single step Nucleophilic addition as shown in Scheme 1.



Scheme 1: Synthesis of receptor FBH-AP

The final structure of the FBH-AP was confirmed by the usual IR, NMR (^1H and ^{13}C), and MASS spectrum. IR: (KBr, cm^{-1}) 3368, 2860, 1704, 1614, 1472, 1107, 1035. ^1H NMR (CDCl_3 / TMS): δ 1.21 (CH₃, t, 3H), 1.83 (C-Me, s, 3H), 2.64 (N-Me, s, 3H), 3.94 (CH₂, s, 2H), 4.21 (CH₂, q, 2H), 7.29 (NH, s, 1H), 7.32 (Ar-phenyl, m, 9H), 7.86 (=CH, s, 1H). ^{13}C NMR (CDCl_3 / TMS): δ 10.25 (–C-CH₃), 14.10 (–CH₂CH₃), 37.09 (N-CH₃), 44.23 (N-CH₂), 61.04 (O-CH₂), 115.08–140.67 (Aromatic), 162.09 (ketone, C=O), 167.50 (ester, C=O). The proton of secondary amine appears at the aromatic region, merged with phenyl protons.

3.2 Fluorescence spectra of FBH-AP

The excitation wavelength of the receptor with different metal ions is standardized at 288 nm by using UV-Vis spectrometer. The binding ability of receptor FBH-AP in the presence of Al^{3+} , Cr^{3+} , Ca^{2+} , Cu^{2+} , Cd^{2+} , Co^{2+} , K^+ , Mg^{2+} , Mn^{2+} , Fe^{3+} and Fe^{2+} are tested in DMF/ H_2O (1:9 v/v) medium by using fluorescence spectrum. Receptor FBH-AP exhibits an emission peak at 388 nm and the addition of above metal ions induced almost no considerable changes in the emission intensity Al^{3+} as an exception are displayed in Fig. 1. Only the addition of Al^{3+} with FBH-AP showed the fluorescence quenching compared to the strong fluorescence of FBH-AP and with other metals. Therefore, the fluorescence emission demonstrated that FBH-AP functions as a highly sensitive and selective fluorescent chemosensor for Al^{3+} .

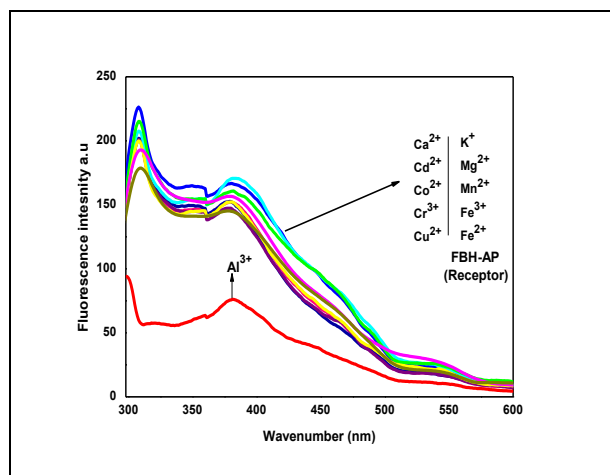


Fig. 1: Fluorescence emission spectrum of FBH-AP with various metal ions

3.3 Selectivity of FBH-AP

Selectivity is an important characteristic of an ion-selective chemosensor (Geddes, C.D., Lakowicz *et al.*), experiments on the Al^{3+} selectivity from mixtures of different metal ions were carried out. Fig. 2 showed the fluorescence emission spectra in the presence of Al^{3+} , the fluorescence intensity of FBH-AP decreases to the minimum, however, most of the other metal ions do not cause any fluorescence quenching because of their open shell d-orbitals. These results showed a strong selectivity of compound FBH-AP for Al^{3+} over all other metal ions.

3.4 Jobs plot

The binding stoichiometry was determined using Jobs plot analysis on continuous varying the mole fraction of FBH-AP with Al^{3+} . The testing was executed in an aqueous solution by varying the total concentration of Al^{3+} from 1×10^{-6} to 1×10^{-4} M to the constant FBH-AP concentration. The plots Fig.3 depicts that the binding

stoichiometry of Al^{3+} with FBH-AP a fluorescence showed a higher value of 0.5 which directed the 1:1 (FBH-AP: Al^{3+}).

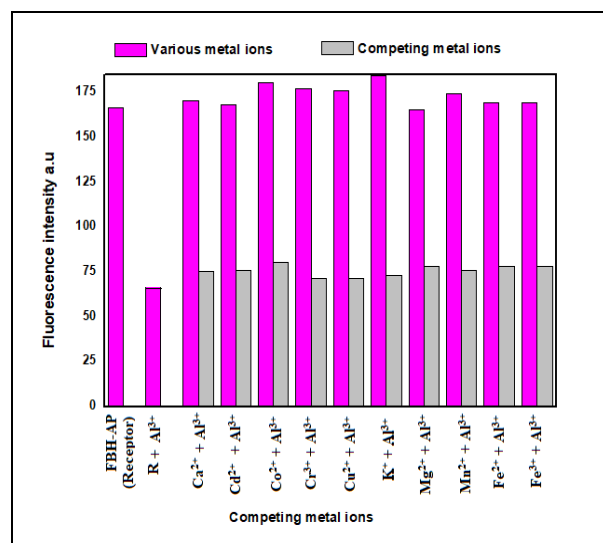


Fig. 2: Competitive study of other metal ions with Al^{3+}

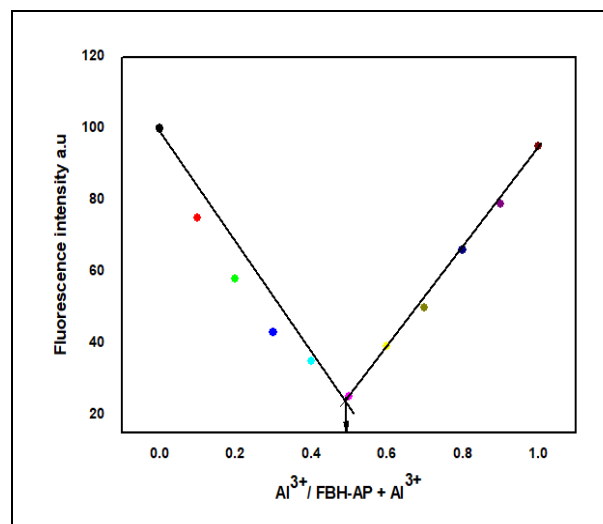
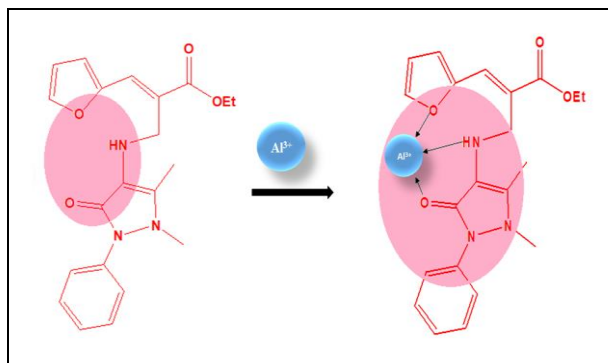


Fig. 3: Jobs plot analysis of FBH-AP with Al^{3+}

3.5 Proposed binding interaction of FBH-AP

Based on the above results a possible mechanism is shown in Scheme 2. As per the design of the chemosensor, it has three heteroatoms containing a lone pair of electrons in the furfural ring 'O' and the antipyrine 'N' and 'O' that are connected covalently through an unsaturated carbon-carbon ($\text{C}=\text{C}$) double bond with extending conjugation. This conjugation is responsible for the photo-induced electron transfer process (PET) (You *et al.* 2012). The heteroatom moiety possesses a strong electron-donating ability and enhances the electron density of the receptor, which makes FBH-AP, displays a strong fluorescence emission. Hence upon complexation of Al^{3+} with FBH-AP, the lone pair of

electrons is involved in bonding with the electron-deficient Al^{3+} decreases the fluorescence intensity. It is because the bonding FBH-AP with Al^{3+} weakens the electron-donating ability of the hetero atoms. As a result, the fluorescence intensity of FBH-AP with Al^{3+} is almost quenched.



Scheme 2: Proposed binding mode of FBH-AP with Al^{3+}

4. CONCLUSION

In summary, we report a new furfural ring cycle of Baylis Hillman adduct with Antipyrine receptor FBH-AP as a fluorescent chemosensor for Al^{3+} ions. The receptor FBH-AP behaves as a highly selective and sensitive chemosensor for the recognition of Al^{3+} over the other metal ions without any interference. The 1:1 complex formation, stoichiometry have been established by the jobs plot method. The binding mode of the FBH-AP with Al^{3+} has been followed by the PET mechanism. The quenching in fluorescence of the receptor FBH-AP when it binds with Al^{3+} can be used for the detection of the Al^{3+} ions. Hence, the receptor FBH-AP could be used as a potential probe to detect Al^{3+} in biological and environmental monitoring works.

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